

IMPACT OF HIGH-TEMPERATURE FOOD PROCESSING ON FATS AND OILS

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1. ABSTRACT

Fats and oils are heated at high temperatures during baking, grilling and pan frying; however, deep fat frying is the most common method of high temperature treatment. Deep fat frying is a popular food preparation method because it produces desirable fried food flavor, golden brown color and crisp texture. For example, in the U.S. in 1994, approximately 12 billion pounds of fats and oils were used with 5.5 billion pounds used for frying and baking (USDA, 1995). Fried snack foods accounted for 2.9 billion pounds of oil, whereas 2 billion pounds were used for frying in restaurants (USDA, 1995). Because of such large consumption of frying oils and fats, the effects of high temperatures on these oils and fats is of major concern both for product quality and nutrition. This chapter will discuss the process of frying and the chemical and physical reactions that occur. The products formed from these reactions will be reviewed as well as information on the effects of the products and the control of these deteriorative reactions.

2. INTRODUCTION

Toxicants that are detected in food can be present naturally or can occur from changes during harvesting, processing, or preservation. They can be further categorized as 1) naturally occurring compounds such as nutmeg; 2) compounds that can be removed by processing such as trypsin inhibitors or aflatoxin; 3) compounds that cannot be removed such as in some seafood and 4) compounds produced by preservation and processing such as in cured meats and in fried food (Morton, 1977). Thermal processing of foods can have positive and negative effects. For example, trypsin inhibitors in soybeans are inactivated

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during a steaming process to produce products that are safe to consume. In addition, high temperature processing can contribute desirable flavors to foods such as roasted coffee, caramel, or fried food. On the other hand, high temperatures may also cause excessive formation of compounds that negatively affect color and flavor in foods such as canned vegetable and fried foods.

3. CHANGES IN OILS AND FOOD DURING DEEP-FAT FRYING

During frying, at approximately 190°C, as oils thermally and oxidatively decompose, volatile and nonvolatile products are formed which alter functional, sensory, and nutritional qualities of oils. Scientists have extensively reported on the physical and chemical changes that occur during frying and on the wide variety of decomposition products formed in frying oils. Physical and chemical changes in oils that occur during heating and frying are presented in Table 1. Specific methods exist to quantitatively measure degradation processes and products, for example, free fatty acids, carbonyl compounds, and high molecular weight products. In addition, decreases in unsaturation, flavor quality, and essential fatty acids can be monitored. However, some physical, qualitative changes in the oil can also be determined subjectively by visual inspection such as increased viscosity, color, and foaming as well as decreased smoke point. Some frying operations, such as in restaurants, discard frying oils when frying causes excessive foaming of oil, when the oil tends to smoke excessively, or when the oil color darkens. In addition, abused oil increases in off-odors such as acrid and burnt and fried food develops off-flavors. There are five stages in the life cycle of a frying oil that generally correspond to the five phases of frying oil deterioration—induction, peroxide formation, peroxide decomposition, polymerization, and degradation—that are based on the chemical reactions that occur during frying. The first stage of the cycle begins when the oil is fresh and is chemically known as the induction phase. Oils in this phase provide little browning and in fact, the food may look undercooked. Fried food flavor intensity is also low. The oil is actually at peak performance during the second phase of the cycle which is the peroxide formation stage. Food has a desirable golden brown color; is fully cooked; and has moderate (optimum) fried flavor. During the third part of the cycle, peroxides decompose and the oil is lower in quality than at the second stage. Food has a darker brown color and a lower fried food flavor intensity than at the previous stage. Off-flavors may be detectable at this phase. By the fourth stage, the oil has begun to polymerize and the oil quality is marginal. Food has a dark brown color and off-flavors; and the oil has begun to foam. By the time an oil reaches phase five, severe oil degradation is occurring and the oil should be discarded. Food has an unacceptable flavor and may not be fully cooked in center because foaming of the oil has limited the direct contact of oil and food. Nonvolatile decomposition prod-

Table 1. Effects of physical and chemical changes during deep fat frying

Physical changes	
Increased:	viscosity, color, foaming
Decreased:	smoke point
Chemical changes	
Increased:	free fatty acids, carbonyl compounds, high molecular weight products
Decreased:	unsaturation, flavor quality, essential fatty acids

ucts eventually produce these physical changes in frying oil—increases in viscosity, color, and foaming (Perkins, 1967). Chemical changes during frying increase free fatty acids, carbonyls, and polymeric compounds and decrease fatty acid unsaturation.

4. PHYSICAL AND CHEMICAL REACTIONS OCCURRING DURING HEATING AND FRYING

Deep fat frying is a complex process with many physical and chemical reactions occurring simultaneously. Frying oils not only transfer heat to cook foods but also help produce distinctive fried food flavor and unfortunately, undesirable off-flavors if the oil is deteriorated. During deep-fat frying, various deteriorative chemical processes such as hydrolysis, oxidation, and polymerization take place and oils decompose to form volatile products and nonvolatile compounds (Figure 1). As heat is transferred from the oil to the food, water is evaporated from the food and oil is absorbed by the food. In addition, the oil is aerated with oxygen as food is added. This process helps enhance one of the major chemical reactions occurring during frying—oxidation. Primary oxidation products—hydroperoxides—are rapidly formed and cleave to alkoxy and hydroxy free radicals that are very unstable at 190°C (Figure 2). Free radicals will react with other compounds to form secondary oxidation products such as aldehydes, alcohols, ketones and hydrocarbons. As water is added to the oil, usually through the addition of food, hydrolysis occurs. Free fatty acids are formed in addition to diglycerides and monoglycerides as the triglyceride decomposes (Figure 3). Polymerization of the oil takes place with the formation of many compounds including dimers, trimers and polymers (Figure 4). The complex process of formation and degradation of volatile and nonvolatile compounds is shown in Figure 5 along with some of the physical changes in the frying oil. With continued heating and frying, these compounds further decompose until breakdown products accumulate to the level that the oil is no longer suitable for use because high levels of these compounds produce off-flavors and potentially toxic effects.

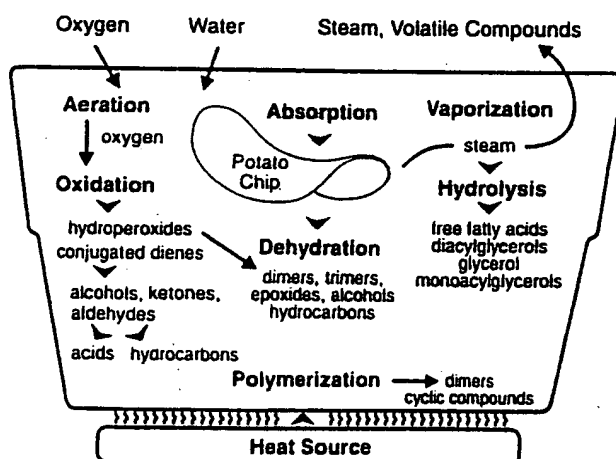


Figure 1. Physical and chemical reactions and products during deep fat frying.

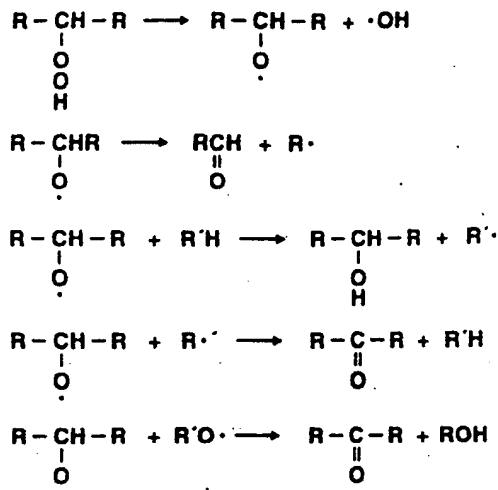


Figure 2. Oxidation reactions and products during deep fat frying.

4.1 Hydrolysis

As food is fried in oil, air and water initiate a series of interrelated reactions. Water and steam hydrolyze triglycerides which produces monoglycerides and diglycerides, and eventually free fatty acids and glycerol (Figure 3). The extent of hydrolysis is a function of oil temperature, interface between oil and aqueous phases, and amount of water and steam since water will hydrolyze oil more quickly than steam (Pokorny, 1989). Free fatty acids and low-molecular weight acidic products from oxidation enhance hydrolysis in the presence of steam during frying (Pokorny, 1989). Hydrolysis products decrease the stability of frying oils and can be used as one measure of oil fry life.

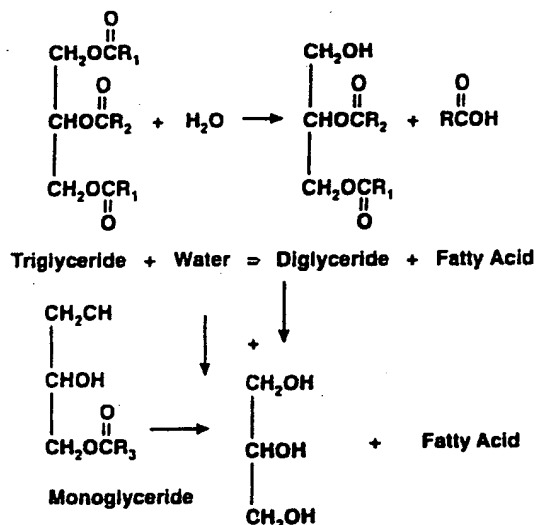


Figure 3. Hydrolytic reactions and products during deep fat frying.

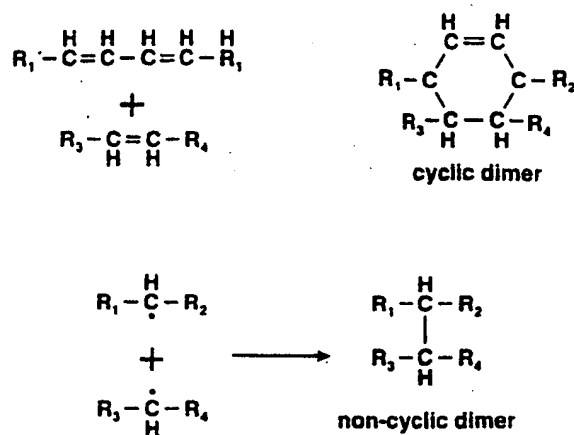


Figure 4. Polymerization reactions and products during deep fat frying.

4.2 Oxidation

Oxygen that is in the oil or that is incorporated with food causes reactions that form volatile and nonvolatile decomposition products. The oxidation mechanism in frying oils is similar to autooxidation at ambient temperature; however, unstable primary oxidation products—hydroperoxides—decompose rapidly at 190°C into secondary oxidation products such as aldehydes (Figure 2). These volatile secondary oxidation products can significantly contribute to the odor of the oil and flavor of the fried food. Analysis of highly volatile products such as hydroperoxides at any one point in the frying process provides

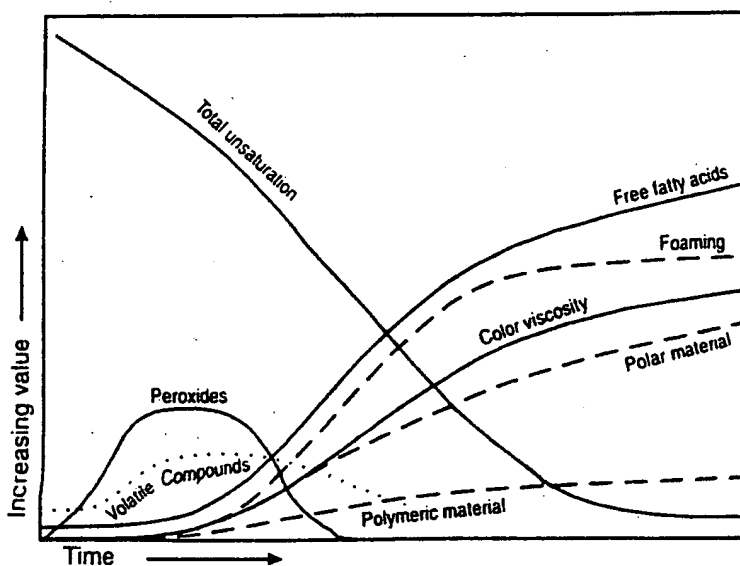


Figure 5. Formation and degradation of compounds in frying oils.

little information since their formation and decomposition fluctuate quickly. During frying, oils with polyunsaturated fatty acids such as linoleic acid have a distinct induction period of primary breakdown products—hydroperoxides—followed by a rapid increase in peroxide values, then a rapid destruction of peroxides (Perkins, 1967; Wessels, 1983). Therefore, monitoring peroxides is not a good indication of the state of the oil. Oxidative degradation produces oxidized triglycerides containing hydroperoxide-, epoxy-, hydroxy-, and keto- groups and dimeric fatty acids or dimeric triglycerides (Wessels, 1983). Volatile degradation products are usually saturated and monounsaturated hydroxy-, aldehydic-, keto-, and dicarboxylic- acids; hydrocarbons; alcohols; aldehydes; ketones; and aromatic compounds (Perkins, 1996).

4.3. Polymerization

Frying produces compounds with high molecular weight such as polymers that can form from free radicals or triglycerides by the Diels-Alder reaction (Figure 4). Cyclic fatty acids can form within one fatty acid; dimeric fatty acids form between two fatty acids, either within or between triglycerides; and polymers are obtained as these molecules cross-link. Oil viscosity increases as the amount of polymerized material increases. Polymerization products decrease the stability of frying oils and can be used to measure oil fry life.

5. FORMATION OF NONVOLATILE AND VOLATILE DEGRADATION PRODUCTS

The extent of thermal degradation of frying oil is affected by unsaturation of fatty acids, frying temperature, oxygen absorption, metals, and food type (Arroyo et al., 1992). Other factors affecting hydrolysis, oxidation, polymerization and frying oil deterioration are presented in Table 2. The type of food being fried can affect the resulting composition of the frying oil as fatty acids are released from fat-containing foods such as chicken. Breaded/battered food can degrade frying oil more quickly and decrease stability compared to uncoated food. Accumulation of degradation products in the frying medium and their incorporation in fried foods is of concern when frying is conducted under abusive conditions (Clark and Serbia, 1991). Combinations of these degradation factors (Table 2) determine the rate of reactions, for example, in one operation, the rate of hydrolysis may be twice that of the rate of oxidation, whereas in another operation with different conditions, the reverse may occur (Fritsch, 1981).

Table 2. Factors affecting frying oil degradation

Oil/food	Process
Unsaturation of fatty acids	Oil temperature
Type of oil	Frying time
Type of food	Aeration oxygen absorption
Metals in oil / food	Frying equipment
Initial oil quality	Continuous or intermittent heating or frying
Degradation products in oil	Frying rate
Antioxidants	Heat transfer
Anti-foam additives	Turnover rate; addition of makeup oil. Filtering of oil / fryer cleaning

Table 3. Volatile compounds in french fried potatoes and frying oils

Frying oil		French fried potatoes	
Butanal	t2,t4-Heptadienal	Hexanal	Decanal
Hexane	2t,4-Heptadienal	Methyl pyrazine	2-Decenal
1-Butanol	2-Octenal	2-Hexenal	2,c4-Decadienal
Pentanol	Nonanal	2-Heptanone	Undecanal
Heptane	2-Nonenal	Nonane	2,t4-Decadienal
Hexane	Decanal	Heptanal	Nonanal
2-Hexenal	1-Decene	2,5 Dimethylpyrazine	2-Octenal
2-Heptanone	3-Octanone	2-Heptenal	t2,t4-Heptadienal
Nonane	2-Decenal	2-Pentylfuran	Octanal
Heptanal	2,c4-Decadienal		
2-Heptenal	Undecanal		
2-Pentylfuran	2,t4-Decadienal		
Octanal	2-Octen-1-ol		
2-Undecenal	Dodecanal		

5.1. Volatile and Nonvolatile Degradation Products

Frying oils degrade to form volatile and nonvolatile decomposition products (Figure 5). Although volatile compounds are primarily responsible for flavor—both positive and negative, thermal polymers do not affect flavor directly. Foods fried in these deteriorated oils may contain a significant amount of decomposition products to cause potential adverse effects to safety, flavor, oxidative stability, color and texture of the fried food. Conditions that produce polymers are not usually encountered in well-managed commercial operations because of practices such as make-up oil addition and monitoring of frying conditions.

Perkins (1996) found several hundred volatile compounds in frying oil and french fried potatoes. The major compounds, listed in Table 3 in the order of elution on a nonpolar capillary column, include aldehydes, ketones, alcohols and hydrocarbons. At lower levels, many of these compounds can contribute to a positive flavor in fried foods; however, at higher levels they may contribute to undesirable off-flavors. Selke et al. (1977) identified volatile compounds and their precursors from heated soybean oil, using triglycerides (triolein, 25% triolein/75% tristearin, and a randomly esterified triglyceride of stearic and 25% oleic acids) heated at 192°C in air for 10 minutes. Each lipid system produced the same major compounds (heptane, octane, heptanal, octanal, nonanal, 2-decenal, and 2-undecenal) that were unique to the oxidation of the oleate fatty acid in each triglyceride sample. Selke et al. (1980) also analyzed pure trilinolein and mixtures of trilinolein-tristearin, trilinolein-triolein, and trilinolein-triolein-tristearin heated at 192°C in air and found pentane, acrolein, pentanal, 1-pentanal, hexanal, 2- and/or 3 hexanal, 2-heptenal, 2-octenal, 2,4-decadienal, and 4,5-epoxyde-2-enal. 2,4-decadienal is a major decomposition product from linoleic acid and at lower levels can be partially responsible for fried food flavor. At our laboratory, we have monitored 2,4-decadienal in fresh and aged potato chips that were fried in oils with a range of high to low amounts of linoleic acid (Warner et al., 1997). Results showed that potato chips fried in cottonseed oil with 55% linoleic acid had significantly greater amounts of 2,4-decadienal and higher intensities of fried food flavor than potato chips fried in high oleic sunflower oil with only 12% linoleic acid.

Nonvolatile degradation products in used frying oils can include polymeric triacylglycerols, oxidized triacylglycerol derivatives, cyclic substances and breakdown products (Perkins, 1996). Rojo and Perkins (1987) classified the degradation products as polar and

Table 4. Polar compounds (mg/g oil) in high oleic sunflower oils used for frying

Oil	Total polar compounds	Oligomers	Dimers	Oxidized monomers	Diglyceride	Fatty acids
Triglyceride A	17.4	2.1	5.7	6.9	2.0	0.7
Triglyceride B	27.2	5.8	8.6	9.6	2.2	1.0
Triglyceride C	41.5	13.3	12.1	13.0	2.3	0.8

nonpolar polymeric fatty acid methyl esters and monomeric fatty acid methyl esters with unchanged, changed (oxidized, cyclized, isomerized, etc.) and fragmented fatty acid esters. Clark and Serbia (1991) found that large declines in iodine values were needed for a significant amount of polymer formation. Dobarganes and Marquez-Ruiz (1996) reported on the type and quantity of nonvolatile compounds formed in high oleic sunflower oil as it deteriorated during frying (Table 4). The total polar compounds ranged from a moderate level of 17.4% to 41.5% (highly deteriorated). Oligomers, dimers and oxidized monomers increased with increasing polar compounds, whereas the diglycerides and fatty acids remained constant. The type of oil also has a significant effect on the quantities of degradation products produced. Marquez-Ruiz et al. (1995) compared the compounds formed in a polyunsaturated sunflower oil and in a high oleic sunflower oil after 5 hours of frying (Ta-

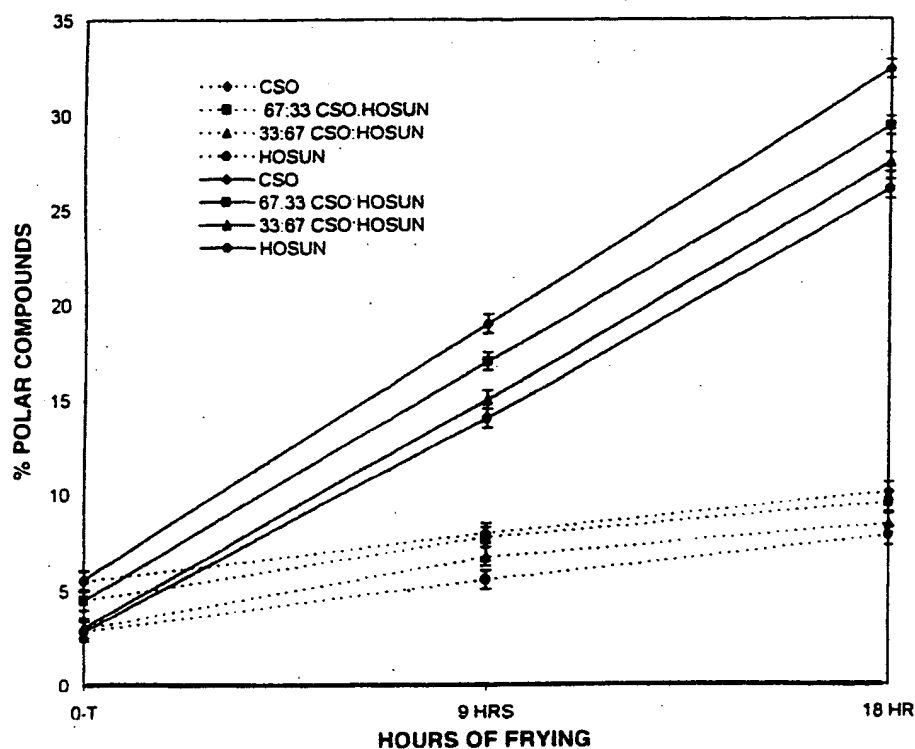


Figure 6. Total polar compound (%) in cottonseed oil (CSO), high oleic sunflower (HOSUN) and blends after 0, 9 and 18 hours of frying french fried potatoes (—) for potato chips (---).

Table 5. Total polar compounds (wt % oil) and polar compound distribution (mg/g oil) of laboratory-used frying oils

Oil	Polar compounds (mg/g)					
	Total (%)	Triglyceride		Oxidized triglyceride monomer	Diglyceride	Free fatty acid
		Polymer	Dimer			
Sunflower	28.9	50.0	125.1	98.0	11.8	4.1
High oleic sunflower	23.0	33.4	82.3	91.3	19.3	3.7

ble 5). As expected the sunflower oil had higher percentages of total polar compounds and of triglyceride polymers, dimers and oxidized triglyceride monomers. Polar compound formation can be altered by frying conditions. In our laboratory, we used the same oils—cottonseed, high oleic sunflower and blends of these two oils—for two types of frying operations (Figure 6). In oils used for potato chips, the polar compound level were at a low level, ranging from 6–8% in oils used for 18 hours primarily because makeup oil was frequently added. On the other hand, oils used for french fried potatoes had much higher polar compound levels. The effect of fatty acid composition was apparent in these oils more than in the potato chip oil because of a lower rate of oil replenishment for the french fried potatoes. Sebedio and Grandgirard (1989) published a review on the minimum and maximum levels of cyclic acids, another type of compound found in frying oils (Table 6). Maximum values ranged widely from 0.16 to 0.66%. Different frying conditions and other variables that affect degradation of oil contributed to this extensive range.

5.2. Feeding Studies

Animal feeding studies have produced a wide range of results depending on the variables used. A review paper by Clark and Serbia (1991) cited a study by Kantorowitz and Yannai (1974) in which soybean oil and hydrogenated soybean oil heated at 200°C were fed to rats (Table 7). Feeding soybean oil heated more than 10 hours retarded growth and had a toxic effect at 43 hours. On the other hand, hydrogenated soybean oil had no adverse effects. Commercially, soybean oil is rarely used for deep fat frying; however, hydrogenated soybean oil is used extensively, so this the use of soybean oil or other polyunsaturated oils in long-term frying tests is mostly of academic interest for comparing with more stable oils. Clark and Serbia (1991) also reported (Table 7) on a 1988 study by Chanin on feeding rats laboratory-heated oil vs. commercial frying oil. The laboratory-heated oils negatively affected weight gain and feed consumption more than the commercial frying oils. As illustrated in previous examples in this chapter, oils from commercial frying op-

Table 6. Cyclic fatty acids in commercial frying

Authors	Amounts (%)		Country	No. of samples
	Minimum	Maximum		
Frankel et al., 1984	0.02	0.50	USA	25
	0.17	0.66	Egypt, Israel	8
Gere et al., 1985	0.02	0.16	Hungary	8
Sebedio et al., 1987	0.01	0.25	France	31
Poumeyrol et al., 1987	0.01	0.09	France	21

Table 7. Laboratory studies of overheated fats and oils

Purpose	Conditions	Results	Reference
Toxicity evaluated in feeding trials of soybean oil (SBO) and hydrogenated SBO (HSBO)	200°C for 10-43hr	SBO with > 10 hr. of heating retarded growth; toxic at 43 hr; HSBO showed no adverse effects; no effects from polymeric fractions	Kantorowitz and Yanni (1974)
Rat feeding of purified diets at 15% for 28 days of lab-heated corn oil and SBO vs double frying of SBO	Thermally oxidized at 200°C vs single and double-fry SBO	Lab heated oils depressed weight gain, feed consumption; commercial SBO comparable to controls	Chanin et al. (1988)

erations usually have much lower degradation than oils abused in laboratory experiments especially when oil is heated without frying.

5.3. Controlling Frying Oil Degradation

What can be done to help provide frying oils and fried foods that are more healthful and with lower levels of deterioration? This can be accomplished to a large extent by controlling the factors (Table 2) that influence frying oil degradation. For example, fresh oil or fat should have good initial quality with no prior oxidation, have low levels of polyunsaturated fatty acids, and have low amounts of catalyzing metals. Metal chelators, antioxidants and anti-foam additives can be added to the oil to help maintain stability and quality (Warner et al., 1985; Frankel et al., 1985). Filtering oils through adsorbents removes carbonized food particles accumulating in the oil along with other oxidation products that limit oil fry life. Controlling frying conditions such as temperature and time, exposure of oil to oxygen, continuous rather than intermittent frying, oil filtration, and turnover of oil will help decrease degradation of the oil. Replenishing with fresh oil is commonly done in frying operations; however, in the snack food industry where more make-up oil is added than in restaurant-style frying, a complete turnover of the oil in the first 8-12 hr of the frying cycle can be achieved (Moreira et al., 1995).

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